*Article*

# Evaluation of Portable X-ray Fluorescence Analysis and Its Applicability as a Tool in Geochemical Exploration

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**Abstract:** Large-scale, high-density geochemical explorations entail enormous workloads and high costs for sample analysis, but, for early mineral exploration, absolute concentrations are not essential. Geochemists require ranges, dynamics of variation, and correlations for early explorations rather than absolute accuracy. Thus, higher work efficiency and lower costs for sample analysis are desirable for geochemical exploration. This study comprehensively analyzed the reliability and applicability of portable X-ray fluorescence (pXRF) spectrometry in geochemical exploration. The results show that pXRF can be applied effectively to rock and rock powder samples, and sample preparation and a longer detection time have been shown to increase the precision of the pXRF results. When pXRF is used on rock samples, if less than 30% of the samples are assessed as containing an element, the element is usually undetectable using pXRF when these rock samples are prepared as rock powders, indicating that the data about the detected element are unreliable; thus, it is suggested that some representative samples should be selected for testing before starting to use a pXRF in a geochemical exploration project. In addition, although the extended detection time increased the reliability of the analysis results, an increase in detection time of more than 80 s did not significantly affect the accuracy of the results. For this reason, the recommended detection time for the pXRF analysis of rock powder samples is 80 s for this study. pXRF has the advantages of being low-cost, highly efficient, and stable, and its results are reliable enough to exhibit the spatial distribution of indicator elements (arsenic, nickel, lead, sulfur, titanium, and zinc) in polymetallic mineralization exploration. Therefore, pXRF is recommendable for practical use in geochemical exploration.

**Keywords:** portable X-ray fluorescence (pXRF); geochemical exploration; mineral exploration; low-cost; in situ detection

## 1. Introduction

Geochemical exploration is an efficient method of mineral exploration [1–4]. It is primarily conducted to determine the elemental concentration and spatial distribution of the elements in various environments (e.g., rock, soil, and stream sediment). To maximize the amount of information about the spatial distribution of elements, geologists tend to attempt to collect more samples at considerably high sampling densities; however, it is costly to process and analyze all the samples collected [2]. Consequently, it is difficult to obtain detailed information about the spatial distribution of indicator elements within a large area. Fortunately, the development of science and technology has continued to improve the performance of scientific instruments and reduce their related costs; the portable X-ray fluorescence (pXRF) spectrometer is an example of such advances [5–9]. pXRF allows geologists to qualitatively or semi-quantitatively obtain the concentrations of a variety of elements in only dozens of seconds [10], thus increasing process efficiency and reducing related costs for large-scale explorations. However, pXRF results are known to vary according to the

detection time of the instrument and the type and water content of the samples [11,12]. The yielded data are assumed to have poor accuracy, and, for this reason, pXRF spectrometry is not widely applied in large-scale mineral exploration projects. However, the relative (i.e., relative to a specific threshold) rather than the absolute concentration of indicator elements could potentially provide valuable geochemical anomaly information for the practical implementation of mineral exploration projects [13–16].

One of the obvious features of conventional laboratory analysis programs is that the sample pretreatment and analysis procedures are time-consuming and require a high level of expertise on the part of the operator. In addition, the sample volume is often very large, so it is inevitable that the samples need to be entrusted to more laboratories for analysis, which poses a challenge to data quality control and the comparison of data from different laboratories. Thus, being able to analyze geochemical samples quickly and easily would be helpful in alleviating the above problems. Many studies have shown that pXRF can be successfully applied to the element content analysis of various matrices, such as vegetation [17–20], soil or sediment [14,21–26], rock [4,27,28], or alloys [29,30]. Although some studies state that pXRF can be applied to the element content analysis of rock samples, the effectiveness and shortcomings of its application in actual geochemical exploration projects have not been systematically evaluated. In order to provide reference for efficient work with pXRF in mineral exploration, it is necessary to evaluate the application of pXRF in the actual geochemical project.

In this study, pXRF was used to estimate the concentrations of elements in rocks and rock powders, and these results were compared to those obtained via laboratory analysis. Some factors which may affect the analytical results were discussed, and the applicability of pXRF in actual geochemical exploration projects was also evaluated.

## 2. Materials and Methods

### 2.1. Study Area and Sampling Method

The study area is located in the Kalatage ore-concentrated area in the East Tian Shan mountains of Xinjiang, China; it is approximately 130 km west of Hami city. The sampling area was located on the southern margin of the Tulufan–Hami Basin. In recent years, several copper–gold–polymetallic deposits have been discovered in the Kalatage ore-concentrated area, including the Red Sea VMS (volcanic-associated massive sulfide) copper–zinc deposit, the Hongshan epithermal copper–gold deposit, the Hongshi–Meilinge epithermal copper deposit, and the Yudai porphyry copper–gold deposit [31,32] (Figure 1).

The sampling area extended approximately 30 km$^2$ beyond the center of the Yudai porphyry copper–gold deposit, which is located in the Gobi Desert. The wide valleys in the study area are covered by Aeolian sand and alluvium, and the thickness of the cover ranges from several centimeters to meters. Additionally, the rocks on the hillside are weathered away, with irregular patterns.

Most of the materials on the surface are affected by Aeolian sand; thus, the sediment is generally considered to be unsuitable for sampling. The rocks were collected along thirteen north–south routes, each of which is approximately 5 km long, with 200-m intervals between each sampling site and 500-m intervals between each route.

### 2.2. pXRF Analysis

An energy-dispersive pXRF (Thermo Fisher Scientific Niton XL3t 950 GOLDD+; Waltham, MA, USA) was used to analyze the 316 rock and rock powder samples. To analyze the rock samples, one piece of rock was randomly selected from each sample, the detection time was set to 120 s, and the MINING Cu–Zn mode was used. To analyze the rock powder samples, all rock samples were ground into a powder with a particle diameter of less than 75 μm. Then, the rock powder samples were packed into snap-and-seal polyethylene sample bags (note that a pile of new empty polyethylene bags was tested to make sure they contained no contaminants for the rock powder samples), and each sample was placed on a mobile test stand. Four maximum detection times were applied (40, 80,

120, and 200 s) under the conditions of the MINING Cu–Zn mode. Each of the four built-in exciter filters in the pXRF spectrometer required a quarter of the total detection time for one sample.
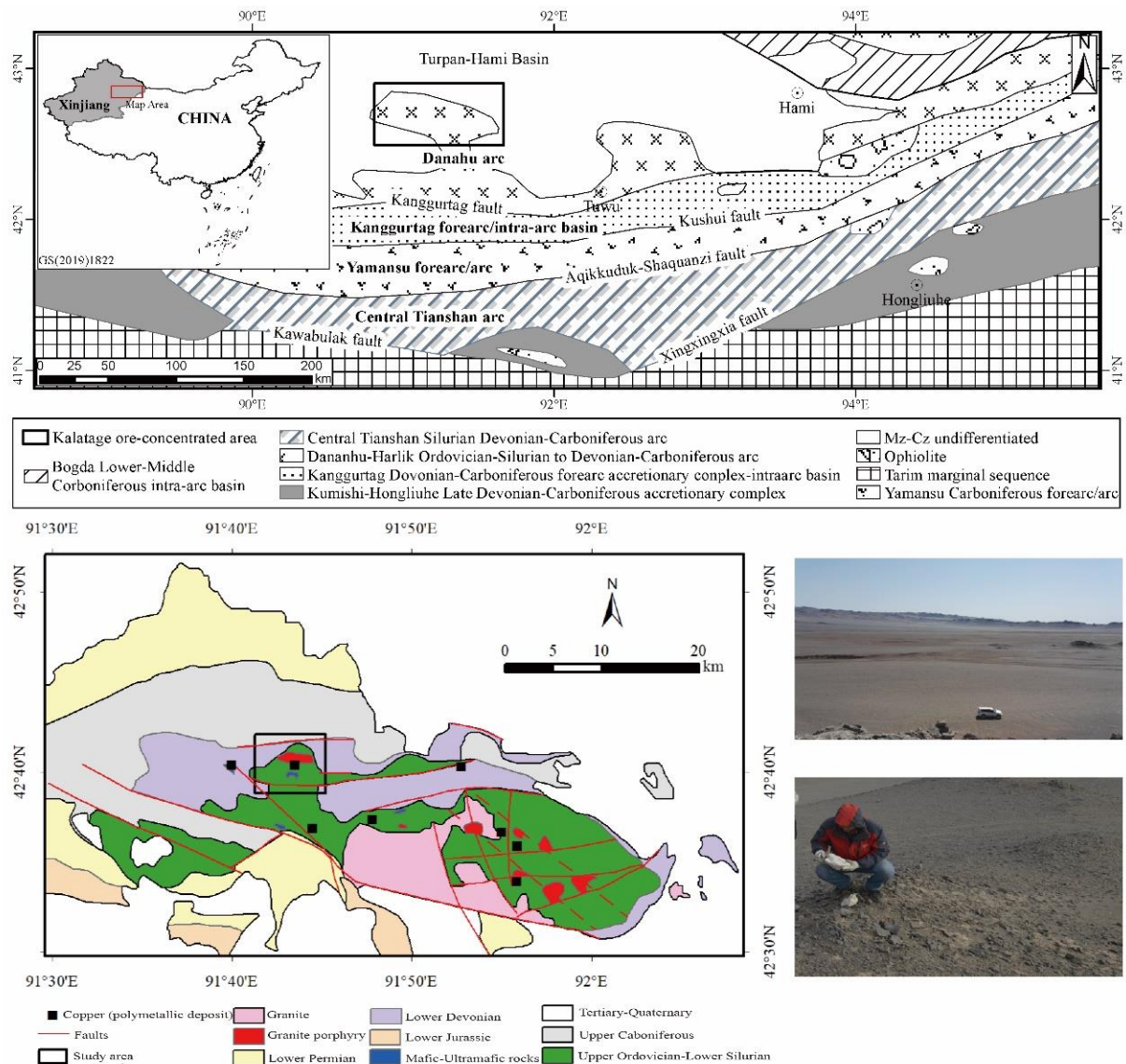


**Figure 1.** Geological map of the study area and the typical landscape (modified from Xiao et al., 2004 [33]; Mao et al., 2018 [31]).

*2.3. Laboratory Analysis*

To determine the concentrations of the elements in the samples accurately, all 316 rock samples were entrusted to a laboratory of the Non-ferrous Geological Exploration Bureau in Xinjiang. Samples were crushed to 75 μm or less, and then the rock powder samples were digested and analyzed according to the methods listed in Table 1.

**Table 1.** List of analytical equipment used to measure the concentrations of the 14 elements.

| Element | Analytical method |
| --- | --- |
| Cd, Co, Cu, Mo, Ni, Pb, Zn | ICP-MS [a] |
| As, Hg, Sb, Ti | AFS [b] |
| Ag, Sn | ICP-OES [c] |
| S | TF [d] |

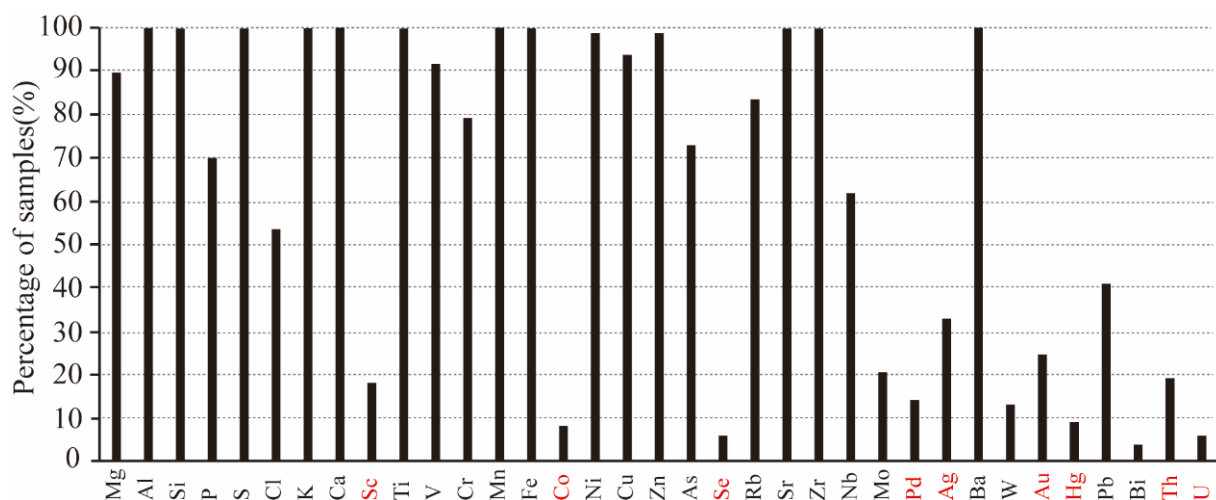[a] ICP-MS, inductively coupled plasma–mass spectrometry; [b] AFS, atomic fluorescence spectrometry; [c] ICP-OES, inductively coupled plasma–optical emission spectrometry; [d] TF, tube furnace method. To monitor the precision of the sample analysis method, four samples by the National Standards of the People's Republic of China (GBW07305a, GBW07312, GBW07360, and GBW07361) were selected as standards in this study, and these standards were inserted into every fifty samples.

## 3. Results

### 3.1. Usability Analysis of pXRF

To investigate the usability of pXRF technology in geochemical exploration, a pXRF was applied to the rocks and corresponding rock powder samples were collected from the study area. The detection time was set to 120 s for the rock samples and 40, 80, 120, or 200 s for the rock powder samples.

A total of 35 elements were identified with pXRF when analyzing the 97 randomly selected rock samples (Figure 2).



**Figure 2.** The percentage of rock samples in which an element could be detected by pXRF.

In total, 26 of the 35 identified elements were measured by operating the pXRF spectrometer in copper–zinc mode to analyze the rock powder samples derived from the above-mentioned 97 rock samples (Figure 3). The results revealed that the detection time could notably affect the results, especially for most of the trace elements. All of the identified elements can be classified into three groups (G1: Mg, Ni, W, and Bi; G2: Al, Ba, Ca, Cl, Si, S, K, V, Ti, Mn, Fe, Rb, Sr, Zn, and Zr; and G3: As, Cr, Cu, Mo, Nb, P, and Pb) according to their different detection times. Very little information was obtained from the G1 group since these elements were only detected in a small percentage of samples. The G2 group was mainly composed of rock-forming elements that could be detected in a detection time as short as 40 s. The G3 group's results indicated that the detection capability increased as the detection time increased. The G3 group's results also indicated that G3 contains perhaps three of the most important geochemical pathfinders for hydrothermal ore deposits: Cu, As, and Mo.
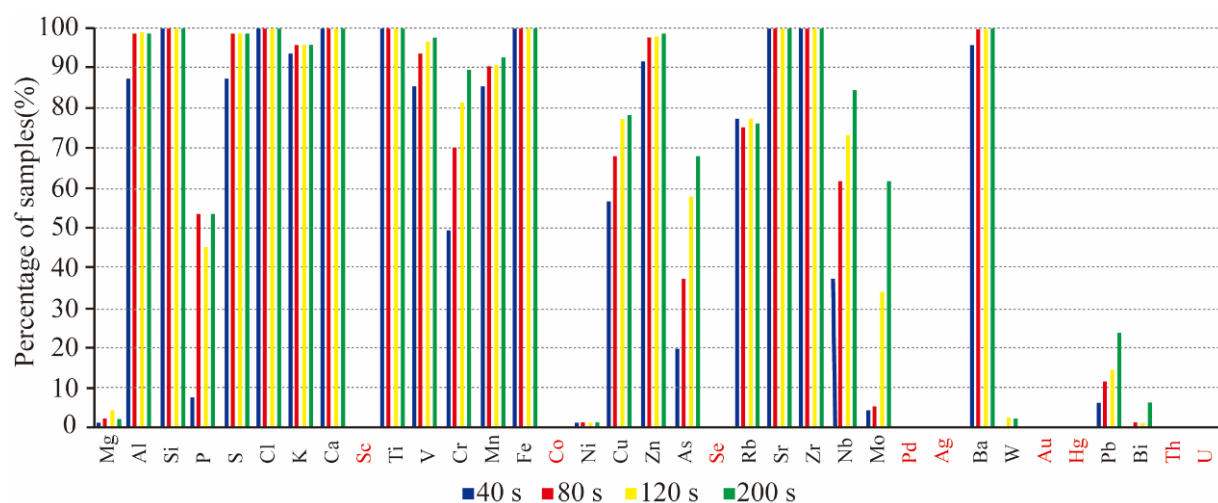
**Figure 3.** The percentage of rock powder samples in which an element can be detected by pXRF based on different detection times.

### 3.2. Influence of Detection Time on Analytical Error

To elucidate the relationship between the detection time and analytical error for each element, four different detection times (40, 80, 120, and 200 s) were applied when the pXRF spectrometer was used to analyze the 97 rock powder samples.

The analytical error results (i.e., two times the standard deviation) were compared based on the detection time for each element detected by the pXRF spectrometer, and the comparative analysis revealed that the analytical error decreased as the detection time increased. The analytical error results for three major elements (aluminum, silicon, and iron) and three trace elements (copper, lead, and zinc) are presented as examples in Figure 4. Table 2 shows that the reduction in the analytical error was most significant when the detection time was increased from 40 s to 80 s, and there is an exponential relationship between the detection time and the analytical error.

**Table 2.** The relationship between detection time and mean analytical error.

| Time　　　　　Element | The Mean Analytical Error of Each Element | | | | | |
|---|---|---|---|---|---|---|
| | **Al** | **Si** | **Fe** | **Cu** | **Pb** | **Zn** |
| 40 s | 2710.91 | 3772.4 | 648.32 | 31.4 | 9.96 | 16.49 |
| 80 s | 866.82 | 1445.5 | 434.67 | 14.85 | 5.4 | 9.45 |
| 120 s | 623.23 | 1010.56 | 340.11 | 14.45 | 4.77 | 8.38 |
| 200 s | 456.99 | 733.31 | 257.27 | 10.52 | 3.35 | 6.26 |
| time(x)-error(y) equation | $y = 2495.8x^{-1.277}$ $R^2 = 0.9768$ | $y = 3601.9x^{-1.174}$ $R^2 = 0.9909$ | $y = 663.13x^{-0.648}$ $R^2 = 0.988$ | $y = 29.483x^{-0.745}$ $R^2 = 0.932$ | $y = 9.7808x^{-0.745}$ $R^2 = 0.9714$ | $y = 16.146x^{-0.666}$ $R^2 = 0.9752$ |

Increasing the detection time from 40 s to 80 s can result in a relatively significant decrease in error, and the error fluctuation also tended to decrease with the increasing detection time (Figure 4). Therefore, it can be stated that the analytical error and its fluctuation is relatively low and acceptable.
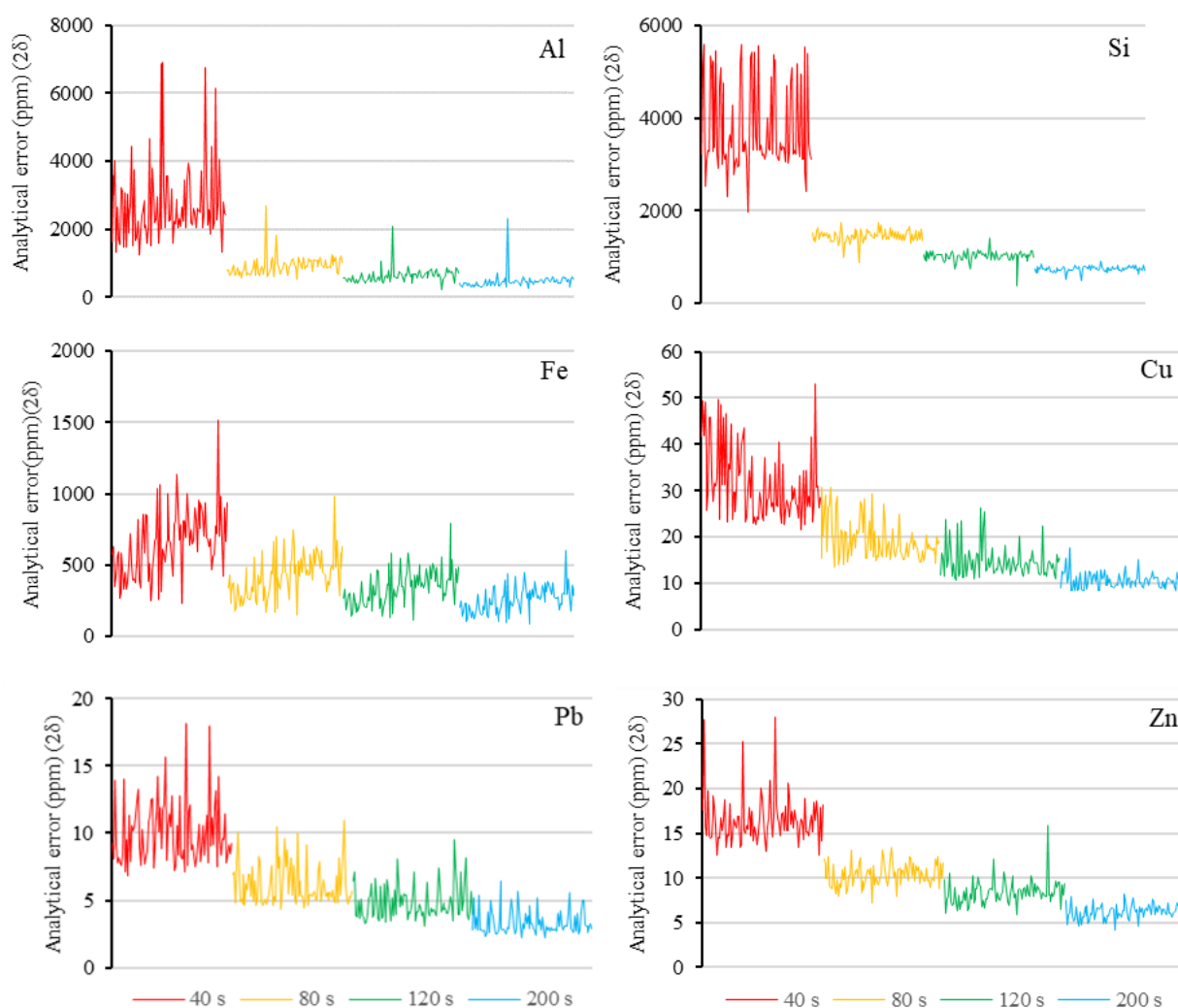
**Figure 4.** Analytical error of rock powder samples by pXRF based on different detection times.

### 3.3. The Reliability and Stability of pXRF

To verify the results of the pXRF-based analysis method, the rock and rock powder sample results were compared to those obtained via laboratory analysis. The results for eight common indicator elements in mineral exploration (i.e., arsenic, copper, molybdenum, nickel, lead, sulfur, titanium, and zinc) are shown in Figure 5.

The result in Figure 5 shows that the reliability of the concentrations via pXRF analysis was not consistent across different elements, with the results for molybdenum being the least reliable. This is because the molybdenum concentration determined via pXRF was imprecise regardless of whether a rock or rock powder sample was used. However, the pXRF-derived results for arsenic, copper, nickel, lead, sulfur, titanium, and zinc were relatively reliable, especially for the rock powder samples. The results for most of the elements (e.g., arsenic and lead) were observed to be more accurate when a longer detection time was applied. However, the extent of the increase in accuracy was modest for most of the elements.

To investigate the robustness of the pXRF results, 32 rock powder samples were randomly selected and individually subjected to three successive rounds of pXRF-based analysis. The correlation coefficient results for these repeated measurements are shown in Figure 6. It can be seen that all the correlation coefficients, except Ni and Cr, were close to one.
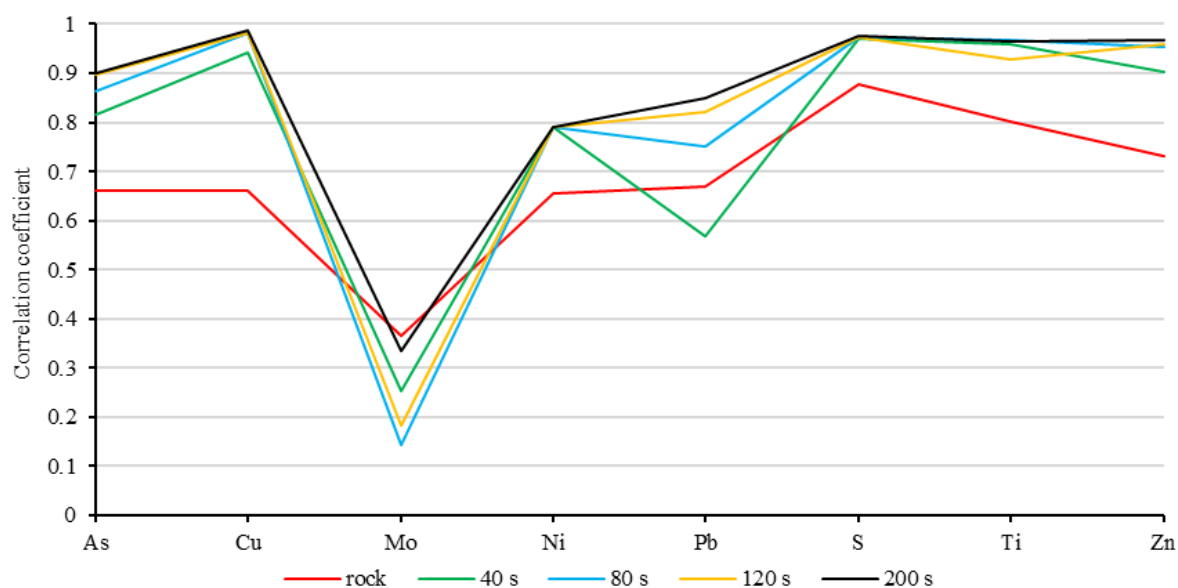
**Figure 5.** Similarity between the analysis results of pXRF and laboratory. The 40 s, 80 s, 120 s, and 200 s are the results of rock powder samples reported by pXRF.
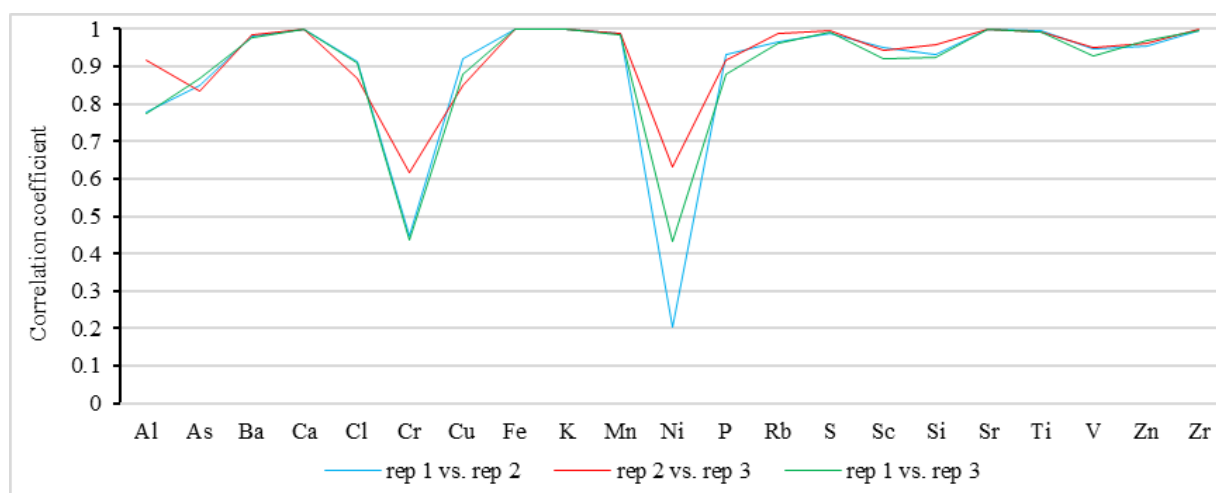


**Figure 6.** Correlation between different repeated measurements of rock powder samples by pXRF.

## 4. Discussion

### 4.1. The Reliability of pXRF

This study demonstrates that the results of applying pXRF to analyze the prepared samples (e.g., rock powder with an average particle diameter of fewer than 75 μm) can be comparable to those obtained via laboratory analysis, which is consistent with other studies [2,34]. Some previous studies have indicated that other factors may also affect the results of pXRF-based analysis (e.g., the water content, sample size, and roughness on the sample surface) [11,12,35]. However, the effect of these factors on the analysis results can be mitigated by simple pretreatment such as natural drying, screening, and/or crushing. Comparison of the pXRF-derived and laboratory analysis-based results for arsenic, copper, nickel, lead, sulfur, titanium, and zinc revealed that those obtained via pXRF-based analyses were generally reliable when the samples were crushed to 75-μm-sized pieces and the pXRF detection time was at least 40 s. Regarding the influence of detection time, previous studies have shown that a longer detection time corresponded to results with higher accuracy and less errors [36]. However, the results from this study demonstrated that the pXRF detection time does not need to be very long because extending it too much will reduce efficiency.

More importantly, and as reported in previous studies, for most of the elements within the detectable pXRF range, the increase in accuracy tends to become less significant as the detection time is increased from 40 s to 200 s [37].

Scholars and geologists should pay attention to the fact pXRF can report some elements (the red labeled elements in Figure 2) when being used on the rock samples that were not reported by pXRF when it was used on the rock powder samples (the red labeled elements in Figure 3). Therefore, it can be stated that although the analytical results of some elements (e.g., As, Cu, Ni, Pb, S, Ti, and Zn) were acceptable in semi-quantitative analysis, the results of the red labeled elements in Figure 2 were inaccurate. Figure 2 also demonstrates that the red labeled elements can only be reported in less than 30% of the total samples, some even less than 20%, and the red labeled elements cannot be reported when the rock samples are prepared as rock powders (Figure 3). Therefore, this study states that the results are unreliable or doubtful when pXRF is used on rock samples if an element can only be reported by pXRF in less than 30% of the total samples.

The various materials (rocks, soils, stream sediments, etc.) taken from the natural environments are usually heterogeneous. In order to obtain more accurate element content, the samples need to be adequately prepared before element content analysis, which is exactly the practice used in conventional geochemical analysis work. Therefore, obtaining accurate analysis results using conventional geochemical analysis is time-consuming and expensive. Unlike conventional methods, pXRF improves efficiency and reduces cost at the expense of the accuracy of the element content analysis. Therefore, pXRF spectrometry is generally considered to be a qualitative or semi-quantitative analytical tool. It should be noted that pXRF analysis results are indeed not as accurate as laboratory analyses, but the application of pXRF makes it possible to analyze more samples, and more data can provide more information, which increases the reliability of the pXRF analysis results.

*4.2. The Geological Significance of the Result*

Taking S, Zn, As and Cu—which are some of the important indicator elements in mineral exploration—as examples, the inverse distance weighted (IDW) interpolation algorithm was used to exhibit their spatial distribution, and the cell sizes of these raster maps were resampled to approximately 200 m according to the sampling density of this study. The results demonstrate that the contents of various elements detected by pXRF are different from the results of laboratory analysis, but different sample analysis methods have little influence on the spatial distribution characteristics of elements, especially for the S, Zn and Cu in Figure 7, where it is difficult to find the differences between the results obtained by different sample analysis methods without careful comparison. Although it is easy to find the differences between the spatial distributions of arsenic obtained by different sample analysis methods, the high-content areas of As-pXRF and As-lab are similar (Figure 7).

A primary goal of geochemical exploration is to identify and delineate anomalous concentrations and spatial distributions of a wide variety of elements in a certain area [2,38]. Therefore, in the case of mineral exploration, it is more important to know the relative concentrations of elements than to obtain very accurate values of the elements in different regions. A pXRF-based analysis can yield reliable results that are adequate to identify the relative elemental concentrations in different regions (Figure 7). Thus, pXRF spectrometry is a reliable tool for the exploration of many kinds of deposits that can be indicated by As, Cu, Ni, Pb, S, Ti, and Zn.
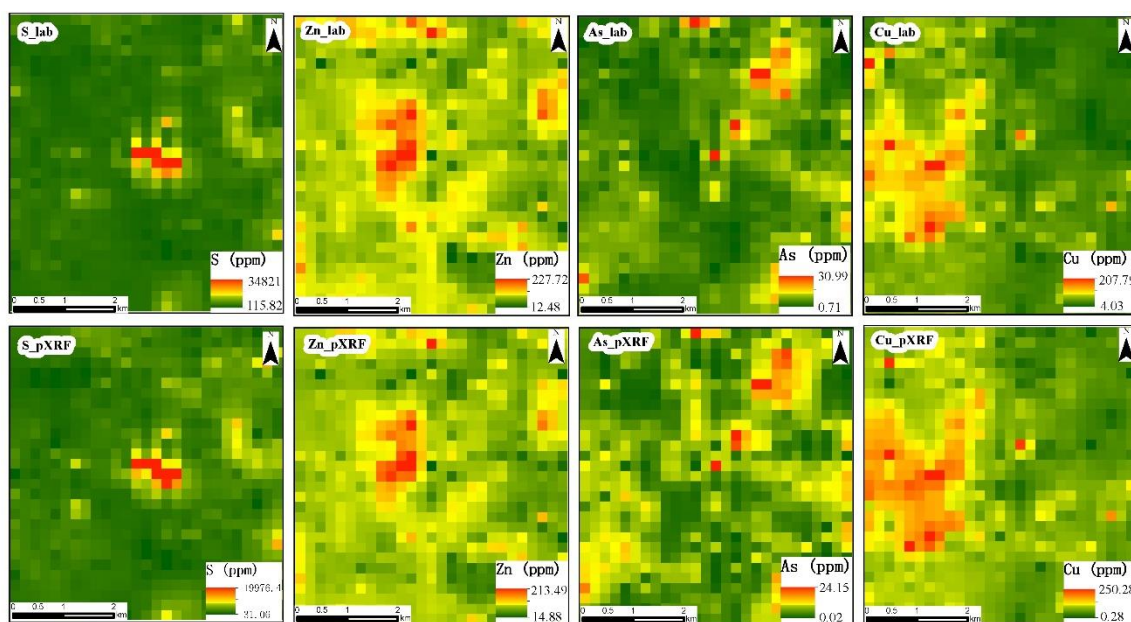
**Figure 7.** Spatial distribution of S, Zn, As, and Cu reported by laboratory (S_lab, Zn_lab, As_lab, Cu_lab) and pXRF (S_pXRF, Zn_pXRF, As_pXRF, Cu_pXRF).

*4.3. The Implications for Further Work*

The results of a few elements (e.g., molybdenum in Figure 5) reported by pXRF are unreliable, but the analytical error tended to decrease with time. Take molybdenum as an example: its content in most of the samples (98.81%) is lower than their abundance in China's continental crust [39,40] according to the data reported by the laboratory. Therefore, if the contents of some elements measured by pXRF are lower than their abundances in the continental crust, the analysis data of these elements cannot provide valuable information for mineral exploration, since they state that there is no metallogenic potential in this region for that element, which is valuable information by itself.

Although many countries in the world, including China, have carried out national scale geochemical explorations, the previous work is insufficient for further mineral exploration. First, the sampling density is relatively low in many of the projects that have been carried out, which is sufficient for the identification of large-scale geochemical anomalies but cannot meet the requirements of identifying small-scale geochemical anomalies and locating ore deposits. Second, geochemical surveys have not been carried out in many countries or regions (e.g., some developing countries or the Turpan–Hami basin, Junggar basin, and Tarim basin in Xinjiang, China). Therefore, there is a large amount of geochemical exploration work that still needs to be carried out in the future, and pXRF can be used in the following ways:

Geologists can collect as many samples as possible in the field. If rocks are being collected and reliable element content is expected, the rocks can be crushed into rock powders; if soils or stream sediments are being collected, the samples can be naturally dried and/or screened according to the specific project, and pXRF can be used on the simply prepared samples directly without the need for digestion, laminating, or melting. A relatively small number of samples can also be selected for accurate analysis based on the results of the pXRF analysis, avoiding blindly entrusting all samples to professional laboratories for analysis.

Note that each of the four built-in exciter filters in the pXRF spectrometer required the same amount of time for detection in this study; however, researchers and geologists may only select one, two, or three of the built-in exciter filters as needed to further improve efficiency.

### 5. Conclusions

1. The pXRF can be used to qualitatively analyze rock samples directly for some elements, especially for elements with relatively high abundances in collected samples, but some results are unreliable when the pXRF is used in anisotropic rock samples. This study shows that the pXRF results are unreliable or doubtful when being used on rock samples if an element can only be reported in less than 30% of the total samples.
2. Although the absolute precision of the analysis may not be sufficient to be used in conventional petrology, the general trends of the pXRF-derived results were consistent with those observed via laboratory analysis. The pXRF results for prepared samples were comparable to those obtained via laboratory analysis for many elements in the detectable pXRF range. Therefore, scholars and geologists are encouraged to include a pretreatment step (i.e., drying, sieving, and/or milling) to improve data analysis and extend the applicability of pXRF spectrometry.
3. The stability of pXRF spectrometry was found to be excellent when it was applied to the elements with high abundance in prepared samples. For most of the elements in the detectable pXRF range, a longer detection time tended to improve the reliability of the results; however, the improvement was not significant for most of the elements when the pXRF detection time was increased beyond 80 s. Thus, an adequate pXRF detection time is suggested to range between 80 and 120 s for powder samples.
4. pXRF spectrometry is a low-cost and efficient technology that can be used to detect the concentrations of dozens of elements in rock powder samples. Thus, pXRF is a practical piece of equipment for geochemical exploration.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author. The data are not publicly available due to other members of our research team will use the data in the near future.

**Conflicts of Interest:** The authors declare no conflict of interest.

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